SWRHL-500r

RECEIVED BY TIC
1971
CONF-710705--5
MASTER

A SEPARATION TECHNIQUE FOR THE DETERMINATION OF KRYPTON-85 IN THE ENVIRONMENT

by
D. L. Stevenson and F. B. Johns
Western Environmental Research Laboratory*

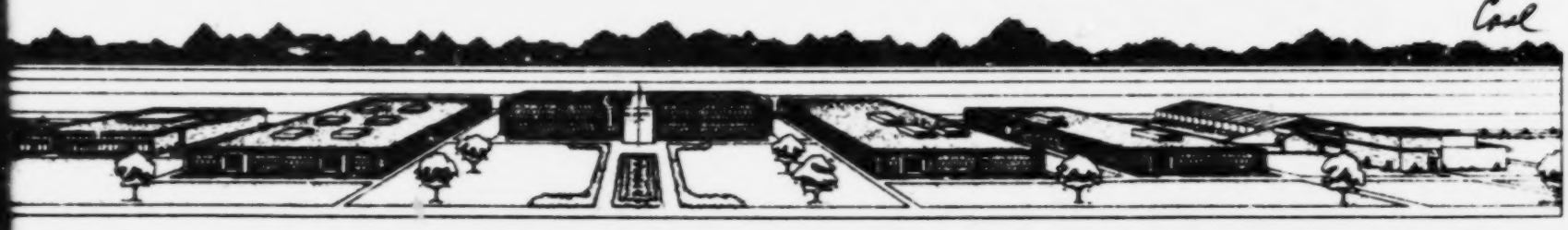
ENVIRONMENTAL PROTECTION AGENCY

Presented at the
International Symposium on Rapid Methods
for Measuring Radioactivity in the Environment
Neuherberg, Germany
July 5-9, 1971

This study performed under a Memorandum of
Understanding (No. SF 54 373)
for the
U.S. ATOMIC ENERGY COMMISSION

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*Formerly Southwestern Radiological Health Laboratory



BLANK PAGE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness or any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Available from the National Technical Information Service,
U. S. Department of Commerce,
Springfield, Va. 22151

Price: paper copy $3.00; microfiche $.95

A SEPARATION TECHNIQUE FOR THE DETERMINATION OF KRYPTON-85 IN THE ENVIRONMENT

D. L. Stevenson and F. B. Johns

Southwestern Radiological Health Laboratory
Environmental Protection Agency
P. O. Box 15027
Las Vegas, Nevada 89114, U. S. A.

INTRODUCTION

Krypton-85 is a by-product of nuclear fission. It is being added to the atmosphere in ever increasing amounts by nuclear reactors, fuel reprocessing facilities, and to a small extent by nuclear weapons tests [1]. Because of the low concentration (1.14 ppm) of stable krypton in the atmosphere, and its properties as an inert gas, krypton presents special analytical problems. Early separations of krypton from air involved the use of stable krypton carrier gas followed by internal gas counting techniques [2]. Sax et al [3] used a series of chemical and combustion reactions to purify krypton which was then counted in a liquid scintillation counter with a solid scintillant. More recently Shuping et al [4] used scintillation solution to absorb krypton gas prior to counting in a liquid scintillation counter.

The procedure described here utilizes a carrier free, chromatographic technique for separating krypton from an atmospheric sample. The krypton is then dissolved and counted in liquid scintillation solution. The method is comparatively simple, reproducible, and sensitive enough to routinely detect environmental levels of krypton-85.

APPARATUS & REAGENTS

The cryogenic-vacuum apparatus (Fig. 1) consists of an all-glass system containing a vacuum manifold and an interconnecting series of traps. The system is designed so that a gas flow can be established from any one trap to another. Inserted in the flow path is a thermal conductivity detector (Gow-Mac model 10-454) with a power supply feeding a strip-chart recorder. Vacuum is supplied by a 130 liter/minute mechanical pump connected to a thermocouple vacuum gauge. A regulated source of helium is used as carrier.

The large charcoal trap (C-1) is filled with 100g of 8-12 mesh activated coconut charcoal. The miniature trap (C-2) contains 0.3g of 30-50 mesh activated charcoal. The three molecular sieve columns (MS-1, MS-2, and MS-3) are made from 150-cm lengths of 9 mm I. D. glass tubing folded to fit inside a one-liter vacuum jar. The columns are filled with Linde type 5Å molecular sieve of 30-60 mesh size.

Tube furnaces are made from cylindrical heating elements wrapped with asbestos and mounted vertically on movable support clamps. The cold baths are 1000-ml vacuum jars mounted like the furnaces. The coolants used in the baths are liquid nitrogen, dry ice-acetone, and ethylene glycol.

The scintillator solution is 5 g of 2,5-diphenyloxazole (PPO) plus 300 mg of 1,4 bis-2-(4 methyl-5-phenyloxazolyl)-benzene (Dimethyl POPOP) dissolved in one liter of scintillation grade toluene (1). The counting vials were fabricated by Don Lillie Inc., Smyrna, Georgia, from borosilicate glass fused to luer fittings. Each vial has an internal volume of about 20 cm^3. Valves, connectors, and caps for luer taper fittings were obtained from the Hamilton Co., Whittier, California. The samples are counted in a Beckman LS-100 liquid scintillation spectrometer operated at room temperature.

PROCEDURE

A sample is collected in the field by using a compressor to fill an evacuated air cylinder. A prefilter and a molecular sieve dryer are inserted on the inlet side of the compressor to remove particulate matter, moisture, and some carbon dioxide from the sample.

(1) Dimethyl POPOP was substituted for the suggested solute bis-MSB[4]. The performance of the two is equally satisfactory in this procedure.

In the laboratory, the cylinder is weighed and then connected to the inlet of the cryogenic-vacuum apparatus. The total sample is leaked into the system using vacuum to maintain a constant differential pressure of one-half atmosphere in the system (2). The gas flow is passed through a calcium sulfate desiccant trap, a trap containing 13x molecular sieve, a cooling coil at liquid nitrogen temperature, and finally to a charcoal trap (C-1) immersed in liquid nitrogen. Vacuum is maintained at the outlet of the charcoal trap until the sample cylinder is evacuated to less than 10 mm Hg. The empty cylinder is then reweighed and the sample size determined.

Oxygen, nitrogen, and argon are removed from C-1 by raising the trap temperature with a dry ice-acetone bath and purging it with helium at a flow rate of 1 liter/minute and 1 atm pressure. The exhaust stream is directed through the thermal conductivity cell which is used to monitor the elution. When the removal is complete, the exhaust flow from C-1 is redirected through the first molecular sieve column (at liquid nitrogen temperature) and finally to vent. Once the flow has been established, the remainder of the sample is transferred to MS-1 by heating C-1 with a tube furnace to 100°C.

The residual components of the sample are selectively eluted from the molecular sieve column by establishing a helium flow rate of about 700cm^3/minute through the column and then raising the column temperature with an ethylene glycol bath precooled to - 15°C. The appearance of individual fractions (Fig. 2) is again monitored by the thermal conductivity detector on a strip-chart recorder. Within two or three minutes after raising the temperature with the glycol bath, the first fraction containing the remaining oxygen and argon is eluted from the column and discarded. The next fraction to appear (6-8 minutes) is krypton which is transferred to a second molecular sieve column held at liquid nitrogen temperature (MS-2). Closely following the krypton is a fraction containing nitrogen and methane which is discarded. The sample is eluted from MS-2 to a third molecular sieve column (MS-3), in exactly the same fashion, with any residues of the undesired oxygen, nitrogen, methane, etc. again being vented (Fig. 3).

The final elution of the purified krypton from MS-3 is directed to a miniature charcoal trap (C-2) immersed in liquid nitrogen. When the transfer is complete, the trap is isolated and the helium carrier gas pumped off the trap by means of vacuum. The trap is then opened to a previously evacuated liquid scintillation vial, and the krypton gas is allowed to expand into the vial by warming C-2 to room temperature. Pressure inside the vial (20-40 mm Hg.) is read from the manometer, the valve is closed, and the vial removed and filled with scintillation solution via a 50-ml luer type syringe. When all of the krypton is dissolved and the vial is full of solution, it is capped and counted along with previously prepared standard and background samples [4]. The volume of krypton in the vial is calculated using the vial volume, manometer pressure, and room temperature. The specific activity of this krypton in

(2) reduced pressure prevents the condensation of liquid air in the trap. A combination of charcoal and liquid oxygen presents a potential explosion hazard [2].

pCi/cm^3 multiplied by the known concentration of krypton in the atmosphere (1.14 cm^3/m^3) yields the activity of krypton-85 per cubic meter of air.

The scintillation solution must be refluxed for 15 or 20 minutes prior to its use to remove dissolved air which prevents absorption of the krypton [4]. The solution should also be slightly warmer than the room or counter temperature when introduced into the vial. Cooler solution will expand causing the vial to leak or break.

To prepare the cryogenic-vacuum system for reuse, the traps are evacuated while being heated to 250-300°C. If samples of high activity are analyzed, the system can be more efficiently decontaminated by alternately flushing the hot traps with helium and then evacuating them.

The procedure requires about four hours per analysis excluding counting time. Environmental samples are routinely counted for 100 minutes each.

RESULTS

Krypton recoveries range from 50 to 70 percent. This yield is based on the volumetric measurement of the recovered krypton compared to the theoretical amount of krypton in the original sample. The purity of 3 typical krypton fractions is shown in table I. Results for the analysis of aliquots from a single, large air sample are given in table II.

The counting efficiency for krypton-85 is 89 percent with a background of 28 counts per minute. Using a sample size of one cubic meter, the sensitivity or minimum detectable activity [5] for this method is less than 2 pCi/m^3 of air.

DISCUSSION

The selection of sample size is primarily a matter of convenience and the sensitivity required. Samples larger than one cubic meter will yield greater sensitivity but are difficult to collect. Very small samples are easy to obtain but may require the addition of stable krypton carrier to facilitate the separation. Nearly all commercially available krypton now contains some krypton-85 contamination. When used as a carrier, this contamination serves to raise the background count rate and consequently reduces the sensitivity of the analysis. For carrier free analysis, the sample size should be at least 0.25m^3 or larger.

The greatest source of error in this method is in the determination of the volume of the purified krypton. If the separation is incomplete, some oxygen and nitrogen may be transferred to the miniature charcoal trap (C-2)

and their volumes measured as krypton. If the helium carrier is not completely evacuated from C-2, it will also be measured as krypton. The presence of these gases serves to reduce the apparent specific activity of the krypton-85.

Other radionuclides do not interfere in the analysis of environmental air samples. If the sample is taken near a reactor site and analyzed within a matter of hours, it may contain krypton-85m (4.4h) and krypton-88 (2.8h) which can be identified by subsequent decay counts.

CONCLUSION

This procedure eliminates the need for krypton carrier, chemical reactions and combustion furances. It is comparatively simple and yet readily detects background levels of atmospheric krypton-85. With minor changes in the conditions, this method can also be used for the separation and counting of atmospheric argon, xenon, and methane.

TABLE I Mass spectrometric analysis (a) of krypton separated from three atmospheric samples

Component	Volume percent		
	1	2	3
Krypton	97.7	98.1	98.1
Oxygen	0.98	0.54	0.53
Nitrogen	0.85	0.77	1.06
Helium	0.23	0.54	-
Hydrogen	0.09	-	-
Methane	0.07	-	-
Carbon Dioxide	0.05	0.07	-
Argon	0.04	-	0.04
C4+ Hydrocarbons	-	-	0.30

(a) Analyses performed by the Chemistry Department of the Lawrence Radiation Laboratory, Livermore, California

TABLE II Replicate analyses of a Homogeneous air sample

Aliquot	Aliquot size(m^3)	Krypton-85 (pCi/m^3)	2-Sigma counting error (pCi/m^3)
1	0.54	12.1	± 2.9
2	0.58	12.0	± 2.3
3	0.41	13.0	± 2.9
4	0.37	12.1	± 3.0
5	0.31	13.4	± 5.4
6	0.37	13.6	± 2.9
7	0.23	11.6	±12.1
8	0.26	12.1	± 4.3

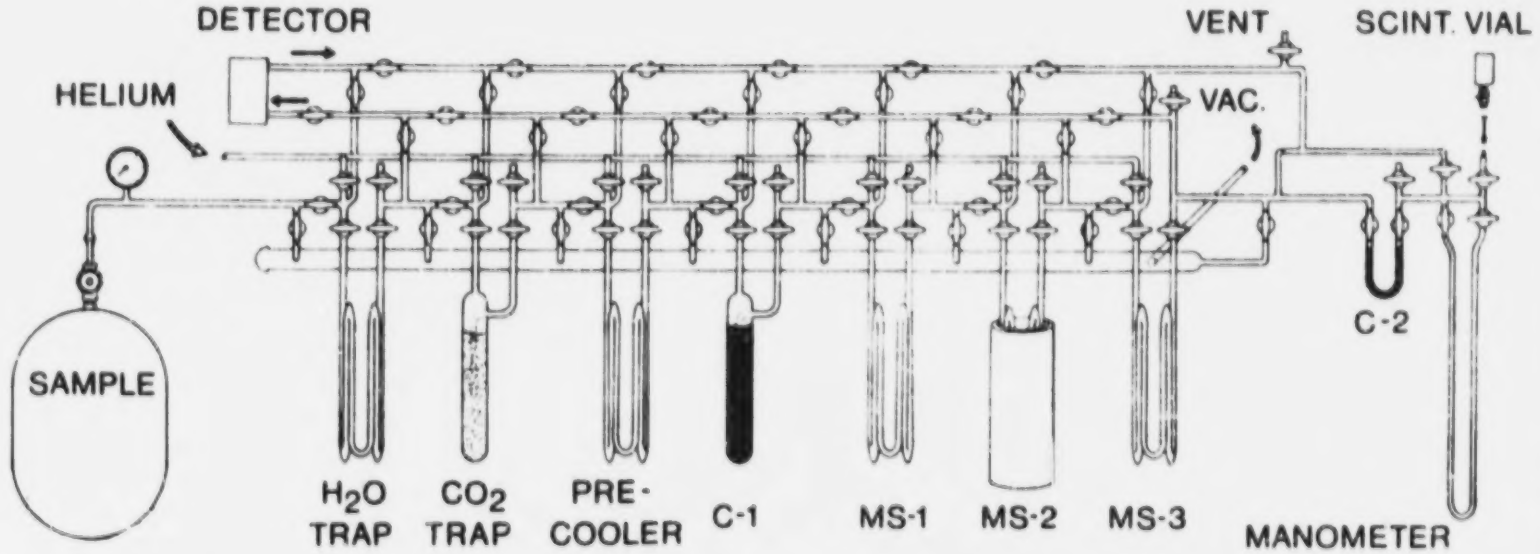
FIGURES

1. Cryogenic vacuum apparatus

2. Elution chromatogram from the first molecular sieve column showing residual air components

3. Elution chromatogram from the second molecular sieve column indicates the removal of unwanted fractions

CRYOGENIC-VACUUM APPARATUS



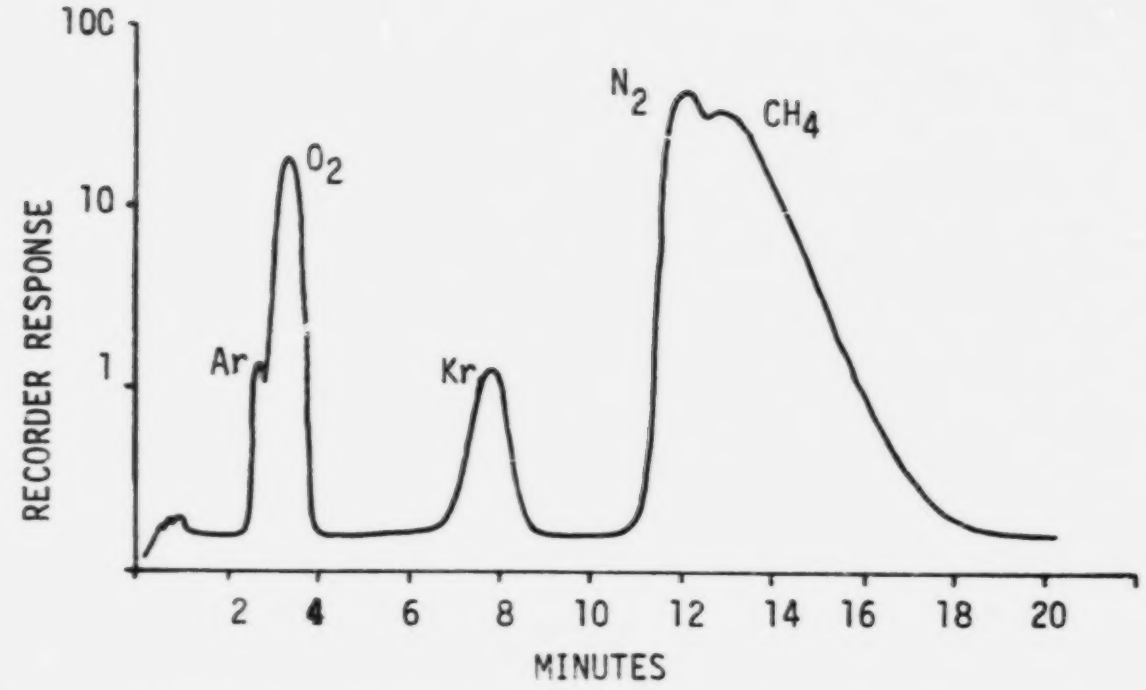


FIGURE 2. Elution chromatogram from the first molecular sieve column showing residual air components.

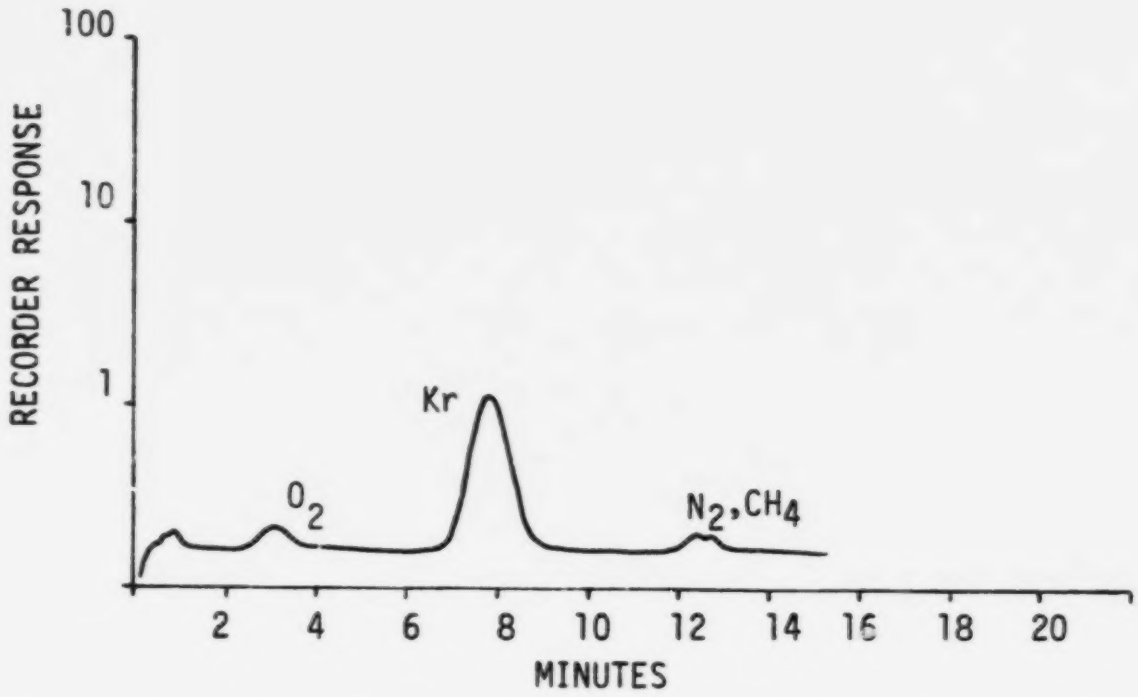


FIGURE 3. Elution chromatogram from the second molecular sieve column indicates the removal of unwanted fractions

REFERENCES

[1] EHHALT, D., K. O. MUNNICH, W. ROETHER, J. SCHOLCH, and W. STICH. Krypton-85 in the atmosphere. Proc. of the 3rd International Conf. on Peaceful Uses of Atomic Energy 14:45-47 (1965)

[2] MOMYER, F. F. The Radiochemistry of the Rare Gases National Academy of Sciences-National Research Council Publication NAS-NS 3025 (1960)

[3] SAX, N.I., R.R. REEVES, and J.D. DENNY. Surveillance for krypton-85 in the atmosphere. Radiol Health Data Rep 10:99-101 (March 1969)

[4] SHUPING, R.E., C.R. PHILLIPS, and A.A. MOGHISSI. Low-level counting of environmental krypton-85 by liquid scintillation. Anal. Chem., 41,2082 (1969)

[5] National Bureau of Standards. A Manual of Radioactivity Procedures, NBS Handbook No. 80 U. S. Dept. of Commerce. 27-28 (1961)